

CA

⑪ ⑬ No. 843985

⑯ ISSUED June 9, 1970



⑫ CLASS 260-476
C.R. CL.

⑩ CANADIAN PATENT

④ STABILIZATION OF ORGANIC MATERIAL WITH
ESTERS CONTAINING AN ALKYLHYDROXYPHENYL GROUP

Martin Dexter, Briarcliff Manor, New York, U.S.A.,
John D. Spivack, Spring Valley, New York, U.S.A., and
David H. Steinberg, Bronx, New York, U.S.A.

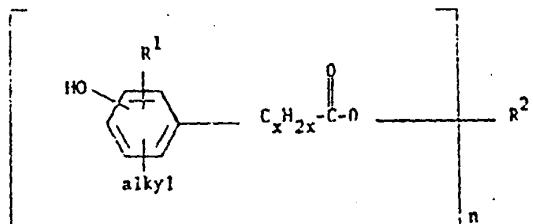
Granted to Geigy Chemical Corporation, Ardsley,
New York, U.S.A.

⑩ APPLICATION No. 861,144
⑩ FILED Oct. 29, 1962

⑩ PRIORITY DATE Oct. 30, 1961 (148,738) Jan. 5, 1962 (164,618) U.S.A.
SUPPLEMENTARY DISCLOSURE filed Nov. 5, 1964

843985

This invention relates to the stabilization of organic material normally subject to oxidative deterioration. More specifically, the invention pertains to a method of stabilizing polypropylene, and other organic material normally subject to oxidative deterioration, with an effective amount of the novel stabilizers of formula I:



in which

R¹ is hydrogen or alkyl,

x is zero or an integer of from 1 to 6,

n is 1 or 2, and

when n is 1, R² is

(i) alkyl of 6 to 24 carbon atoms,

(ii) alkylthioalkyl of 8 to 24 carbon atoms, or

(iii) hydroxyalkylthioalkyl of 8 to 24 carbon atoms,

provided that when x is zero and R² is alkyl, the alkyl group has from 6 to 11 carbon atoms, the hydroxyl group is in the 4-position, R¹ is t-butyl and R¹ and "alkyl" are in the 3- and 5-positions; or

when n is 2, R² is

(i) alkylene of 2 to 6 carbon atoms,

(ii) alklenethioalkylene of 2 to 12 carbon atoms, or

(iii) alkyleneoxyalkylene of 4 to 24 carbon atoms.

Preferably, the "alkyl" group of the phenyl nucleus as well as R¹ are t-butyl groups in the 3- and 5-positions. It is also understood that bulky groups such as t-butyl groups, are not contemplated as being on adjacent carbon atoms of the phenyl nucleus.

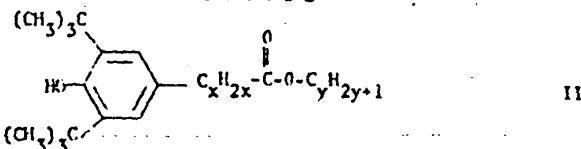
It is a further object of the invention to provide a novel stabilized composition of matter which comprises organic material normally subject to oxidative deterioration with a stabilizer compound of the formula I.

5 Materials which are stabilized according to the invention include polyolefins, especially synthetic resins such as polypropylene and polyethylene. Hydrocarbon material, mineral oil, etc. is also stabilized. Elastomeric material, especially mixtures or combinations of elastomers and other 10 polymers, e.g. high impact polystyrene containing polybutadiene, are all contemplated as materials for stabilization according to the invention.

15 In general, the stabilizers are employed in an amount of from about 0.005% to about 10% by weight based upon the stabilized composition. In polypropylene amounts of from about 0.05% to about 5% by weight are advantageous with from about 0.1% to about 1% by weight being especially preferred. In hydrocarbon oils amounts of from about 0.05% to about 5% by weight are especially useful. In high impact 20 polystyrene 0.05% to 5% by weight of stabilizer is preferred. (All the foregoing percents by weight are based on the stabilized composition.)

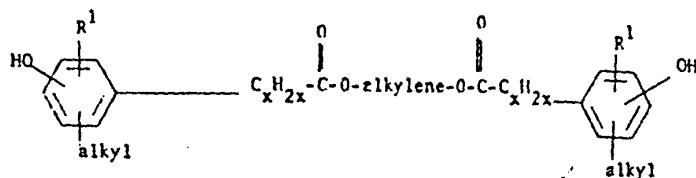
25 Still another object of the invention is to provide novel compounds which are useful in the stabilization of organic material such as, e.g., polypropylene which is subject to degradation. The preferred novel compounds of the invention which are especially useful in stabilizing organic material, in particular, polypropylene, are the compounds of the formula II:

843985



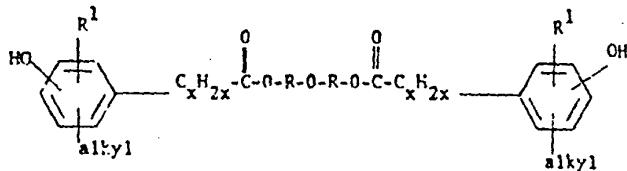
in which R^1 is hydrogen or alkyl, "alkylene-S-alkyl" has from 2 to 12 carbon atoms, and x has a value of from 0 to 6.

The compounds of formula III



in which R^1 is hydrogen or alkyl, "alkylene" has from 2 to 6 carbon atoms, and x has a value of from 0 to 6.

The compounds of formula IV



in which R is alkylene of 2 to 6 carbon atoms, R^1 is hydrogen or alkyl and x has a value of from 0 to 6.

10

Preferred compounds of formula I are those wherein n is 1, x is zero, the hydroxyl is in the 4-position, R^1 and "alkyl" are t-butyl groups in the 3- and 5-positions and R^2 is alkyl of 6 to 11 carbon atoms. These compounds are alkyl 3,5-di-t-butyl-4-hydroxybenzoates. Other preferred compounds of formula I are those wherein n is 1, x is 1 or 2, R^1 and "alkyl" are t-butyl groups in the 3- and 5-positions and the hydroxyl is in the 4-position, i.e. alkyl 3,5-di-t-butyl-4-hydroxyphenylacetates and phenyl propionates.

Preferred compounds of formula II are those wherein the hydroxyl group is in the 4-position on the benzene ring, R^1 and the "alkyl" attached to the benzene ring are t-butyl groups in the 3- and 5-positions and x is zero, 1 or 2.

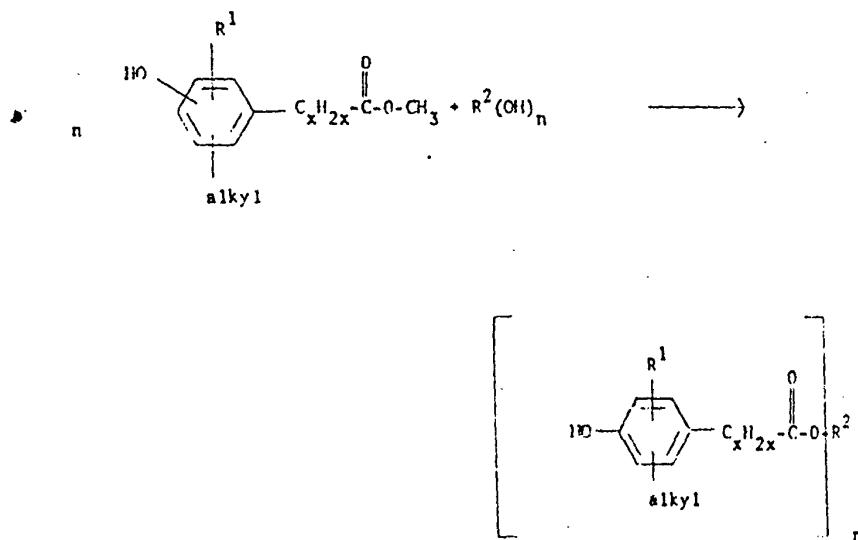
20

843985

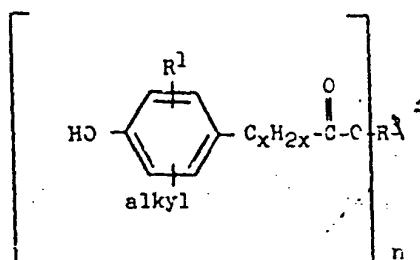
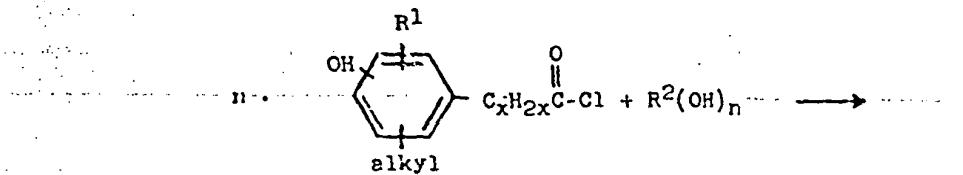
Preferred compounds of formula III are those wherein each hydroxyl is in the 4-position, R^1 and "alkyl" are t-butyl groups in the 3- and 5-positions and x is zero, 1 or 2.

Finally, preferred compounds of formula IV are those wherein each hydroxyl is in the 4-position, R^1 and "alkyl" are t-butyl groups in the 3- and 5-positions and x is zero, 1 or 2.

The compounds of this invention may be prepared in a number of ways. Thus the precursor acids are esterified according to conventional methods as by reaction with the appropriate alcohol in the presence of an acid catalyst, e.g., p-toluenesulfonic acid. In the case of higher alkyl esters, it is often more convenient to employ transesterification, reacting a lower alkyl ester of the acid, such as the methyl ester, with the higher alkanol in the presence of sodium methoxide. Alternatively, the acid chloride of the acid can be employed in esterification procedures. The following reaction schemes illustrate several methods for preparing the compounds of this invention:

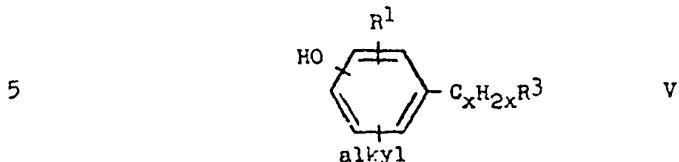


H



in which R^1 , R^3 , x and n are as above defined.

Suitable starting materials include compounds of the formula:



in which R^3 is carboxy, carbalkoxy, carboxyl halide and cyano.

Starting materials of the alcohol reactant type include branched and straight chain compounds having 10 one or two hydroxy groups per molecule. Such alcohols may be substituted with other groups such as with ether

or thioether linkages. Examples of monohydric alcohols thus include heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol and the like. Examples of monohydric alcohols having a thioether linkage include 2-(hexylthio)ethanol, 2-(heptylthio)ethanol, 2-(octylthio)ethanol and the like. Examples of monohydric alcohols containing an ether linkage 2-(hexoxy)ethanol, 2-(heptoxy)ethanol, 2-(octoxy)ethanol and the like.

The compounds of this invention may be used alone or in combination with other stabilizers or additives. Sulfur containing esters of the dialkyl thiodialkanoate type such as dilauryl thiodipropionate are especially useful in certain cases.

Other antioxidants, antiozidants, thermal stabilizers, ultraviolet light absorbers, coloring materials, dyes, pigments, metal chelating agents and the like may also be used with the stabilizers of this invention.

In this specification, the term "stabilization" includes protection not merely against oxidation, degradation,

843985

but also protection against deterioration caused by thermal effects, visible and/or ultraviolet radiation, etc. Thus, the stabilizers of the invention are contemplated as acting to protect unstable materials not only against oxidative deterioration but also against other types of deterioration such as thermal degradation or degradation caused by visible and/or ultraviolet light.

5 The following examples are illustrative of the invention only, and there is no intention to limit the scope of the invention thereto. In the following examples parts are by weight, unless otherwise specified, and temperatures are in degrees centigrade. The relationship between parts by weight and parts by volume is as grams to cubic centimeters.

10

EXAMPLE 1: Methyl 3,5-Di-t-butyl-4-hydroxyphenylacetate

17 Parts of 3,5-di-t-butyl-4-hydroxyphenylacetic acid and 0.5 parts of p-toluenesulfonic acid are dissolved in 200 parts by volume of methanol and heated under reflux for 3 hours. The brown reaction mixture is poured onto crushed ice and the precipitated methyl ester filtered by suction. The filter cake is dispersed in saturated bicarbonate solution, the insoluble is filtered off, washed neutral with distilled water and dried. 17 Parts of crude methyl ester, melting at 79-83°, are obtained. The methyl ester is purified by distillation (b.p. 117-118° at 0.1-0.05 mm Hg) and recrystallization from a mixture of hexane and petroleum ether, melting at 85-86.5°.

	<u>Analysis:</u>	C	H
15	Calculated for $C_{17}H_{26}O_3$ (M.W. 278.3):	73.34%	9.41%
	Found:	73.53%	9.17%

EXAMPLE 2: n-Octadecyl 3,5-Di-t-butyl-4-hydroxyphenylacetate

20 7.2 Parts of methyl 3,5-di-t-butyl-4-hydroxyphenylacetate, 7 parts of n-octadecyl alcohol and 0.1 part of sodium methylate are heated under nitrogen at 130° for 1 1/2 hours. The split-off methanol is swept out with nitrogen and collected in a trap, cooled with dry ice-acetone. After 1.2 parts of methanol are collected, the melt is heated at 150° and 0.05 mm Hg pressure for another 3 hours. The homogeneous melt is dissolved in 40 parts by volume of hexane and cooled for crystallization. The crystalline precipitate, consisting of unreacted n-octadecyl alcohol, is filtered and the filtrate is concentrated under vacuum. The residue weighs 6.6 parts 25 and is purified by high vacuum distillation. After a fore-run, consisting of 2.3 parts of unreacted methyl 3,5-di-t-

843985

butyl-4-hydroxyphenylacetate, 4.3 parts of n-octadecyl 3,5-di-t-butyl-4-hydroxyphenylacetate distill over at 230° and 0.075 mm Hg pressure. The so-obtained n-octadecyl 3,5-di-t-butyl-4-hydroxyphenylacetate, as an oily ester, solidifies on long standing, melting at 33-35°.

Analysis:

	<u>C</u>	<u>H</u>
Calculated for $C_{34}H_{60}O_3$ (M.W. 516.8):	79.17%	11.73%
Found:	78.44%	11.23%

Example 3:

n-Octadecyl β -(3,5-Di-t-butyl-4-hydroxyphenyl)propionate

10 1-Octadecanol (3.63 parts) and 3.75 parts of β -(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid are dissolved in 40 parts by volume of benzene, 0.5 parts of p-toluenesulfonic acid added and the mixture refluxed with stirring for 2 1/2 hours. Approximately the theoretical amount of water (0.34 parts) is collected during this time by azeotroping with benzene into a 5 parts by volume trap. At the end of the reflux period, the brownish solution is cooled, filtered and stripped of benzene in vacuo. The residue (7 parts), which crystallizes on standing, is recrystallized from a 3:2 methanol-ethyl acetate mixture, yielding 4 parts of the n-octadecyl β -(3,5-di-t-butyl-4-hydroxyphenyl)propionate, which is a white, crystalline powder, melting at 49-50°.

20 Analysis:

Saponification Equivalent

Calculated for $C_{35}H_{62}O_3$:	530.9
Found:	526.6

Example 4:

2-(n-Octylthioethyl) 3,5-di-t-butyl-4-hydroxy-benzoate

To a solution of 7.5 parts of 3,5-di-t-butyl-4-hydroxy-benzoic acid and 1.98 parts of potassium hydroxide in

50 parts by volume of methanol, is added a solution of 6.26 parts of 2-chloroethyl-n-octyl sulfide in 30 parts by volume of methanol. The reaction mixture is stirred and heated for 2 hours at 45°. After cooling to room temperature, the reaction mixture is treated with 150 parts by volume of benzene and 200 parts of water. The aqueous layer is extracted with two portions of 75 parts by volume of benzene. The organic solutions are combined and washed successively with two portions of 100 parts of water, three portions of 75 parts of 1 N sodium hydroxide, two portions of 100 parts of water, two portions of 5% hydrochloric acid, two portions of 100 parts of water, two portions of saturated sodium chloride. The benzene solution is then dried over anhydrous sodium sulfate. After filtering and evaporating the solvent, 10.2 parts (80%) of crude product are obtained. Distillation of the crude product yields 2-(n-octylthioethyl) 3,5-di-t-butyl-4-hydroxybenzoate, in a fraction boiling at 206-208° and 0.14 mm Hg pressure and having a refractive index of 1.5128 at 26.5° using the sodium D light.

Analysis:

	C	H	S
Calculated for $C_{25}H_{42}O_3S$:	71.04%	10.02%	7.59%
Found:	71.34%	10.10%	7.08%

EXAMPLE 5: 2-(n-Octylthioethyl) 3,5-Di-t-butyl-4-hydroxy-phenylacetate

A solution is made consisting of 5.22 parts of 3,5-di-t-butyl-4-hydroxyphenylacetic acid, 1.31 parts of potassium hydroxide in 50 parts by volume of methanol. To this solution is added, while stirring at room temperature (25°), a solution of 4.14 parts of 2-chloroethyl-n-octyl sulfide in 20 parts by

volume of methanol. The reaction mixture is stirred at $45^{\circ}\pm 3^{\circ}$ for 3 hours. After cooling, the reaction mixture is diluted with 150 parts by volume of ether and 200 parts of water. After thoroughly mixing, the organic layer is separated and washed successively with water (3 x 100 parts), saturated sodium bicarbonate (4 x 100 parts), water (2 x 100 parts), 5% hydrochloric acid (2 x 100 parts), water (2 x 100 parts), and saturated sodium chloride (1 x 100 parts). The washed ethereal solution is dried over anhydrous sodium sulfate, then filtered and the solvent removed under diminished pressure, leaving a residue of 6.6 parts (76.5%) of 2-(n-octylthioethyl) 3,5-di-t-butyl-4-hydroxyphenylacetate. The product has a boiling point of 207°/0.07 mm Hg and a refractive index of 1.5085 at 27.2° using the sodium D light.

Analysis:

	C	H	S
Calculated for $C_{26}H_{44}O_3S$:	71.52%	10.16%	7.34%
Found:	71.90%	9.73%	7.67%

EXAMPLE X: 2-(n-Octadecylthioethyl) 3,5-Di-t-butyl-4-hydroxyphenylacetate

To a solution of 5.5 parts of 3,5-di-t-butyl-4-hydroxyphenylacetic acid and 1.38 parts of potassium hydroxide in 100 parts by volume of methanol, are added 7.27 parts of 2-chloroethyl-n-octadecyl sulfide. The resulting mixture is warmed for 6 1/4 hours at $50^{\circ}\pm 3^{\circ}$, with stirring. After cooling to room temperature, 200 parts by volume of ether and 300 parts of water are added to the reaction mixture. The aqueous layer is extracted with two additional portions of 75 parts by volume of ether. The combined organic solutions are washed successively with two portions of 100 parts of water, three portions of 100 parts of saturated sodium bicarbonate, two portions of 100 parts of water, two portions

of 100 parts 5% hydrochloric acid, two portions of 100 parts of water, and one portion of 100 parts of saturated sodium chloride. The ether solution is then dried with anhydrous sodium sulfate. After removal of the drying agent, evaporation of the solvent under diminished pressure gives 9.5 parts (80%) of product. The product, 2-(n-octadecylthioethyl) 3,5-di-t-butyl-4-hydroxyphenylacetate, is purified by chromatography on alumina, employing hexane as the eluting solvent.

10	<u>Analysis:</u>	C	H	S
	Calculated for $C_{35}H_{64}O_3S$:	74.94%	11.18%	5.56%
	Found:	75.48%	11.41%	6.11%

H

EXAMPLE 8: 2-(*n*-Octadecylthioethyl) 3,5-Di-*t*-butyl-4-hydroxybenzoate

15 By reacting 7.5 parts of 3,5-di-t-butyl-4-hydroxy-
benzoic acid, 1.95 parts of potassium hydroxide, 10.5 parts
of 2-chloroethyl-n-octadecyl sulfide and 100 parts by volume
of methanol according to the method described in Example 7
hereinabove, the product is obtained in 84% yield. It may be
20 purified by chromatography, using the same conditions as de-
scribed for the compound of Example 7. The product, 2-(n-octa-
decylthioethyl) 3,5-di-t-butyl-4-hydroxybenzoate, is obtained
as a syrup.

<u>Analysis:</u>	C	H	S
Calculated for $C_{25}H_{32}O_3S$:	74.67%	11.10%	5.70%
Found:	74.96%	11.07%	6.52%

9

EXAMPLE 9: 2-Hydroxyethylthio-2'-ethyl (3,5-di-t-butyl-4-hydroxy)benzoate

A mixture consisting of 6.5 parts of methyl 3,5-di-
t-butyl-*h*-hydroxybenzoate, 1.2 parts of bis-(2-hydroxyethyl)-

10 sulfide and 0.108 parts of sodium methylate is heated for
 15 hours at 150-160° with occasional stirring. After cooling,
 the mixture is dissolved in 50 parts by volume of benzene and
 washed with 4 portions of 50 parts of water. After drying over
 20 anhydrous sodium sulfate, filtration and evaporation of
 solvent gives 5.1 parts of crude product. Repeated crystallization
 25 from hexane gives the product, 2-hydroxyethylthio-
 3'-ethyl (3,5-di-t-butyl-4-hydroxy)benzoate, as a white solid
 of constant melting point 114-115°.

10

Analysis:

	C	H	S
Calculated for $C_{10}H_{20}O_4S$:	64.37%	8.53%	9.05%
Found:	64.26%	8.74%	9.48%

15 IIEXAMPLE 19: α,α' -Thiodiethyl Bis-(3,5-di-t-butyl-4-hydroxyphenylacetate)

20 2.8 parts of α,α' -dihydroxydiethyl sulfide, 12.7 parts of methyl 3,5-di-t-butyl-4-hydroxyphenylacetate and 0.1 part of sodium methylate are melted together under nitrogen and heated at 130° for 2 1/2 hours. The split-off methanol is swept out by a stream of nitrogen and caught in a dry-ice trap. The reactants are then heated at 65° and 0.5 mm Hg pressure for 3 hours. The content of the flask is dissolved in warm benzene, the insoluble filtered off and the benzene filtrate washed three times with saturated sodium chloride solution. The yellow filtrate is then dried over anhydrous sodium sulfate and the solvent evaporated under vacuum. α,α' -Thiodiethyl-bis-(3,5-di-t-butyl-4-hydroxyphenylacetate) is obtained by successive crystallization from hexane, a solvent mixture of hexane and tertiary butanol. The product is obtained as white crystals, melting at 117-118°.

<u>Analysis:</u>	<u>C</u>	<u>H</u>	<u>S</u>
Calculated for $C_{36}H_{54}O_6S$:	70.32%	9.86%	5.21%
Found:	70.49%	9.07%	5.03%

Example 10: n-Hexyl-3,5-Di-t-butyl-4-hydroxybenzoate

1.84 Parts of n-hexanol and 1.82 parts of triethylamine are dissolved in 50 parts by volume of dry benzene, and 4.72 parts of 3,5-di-t-butyl-4-hydroxybenzoyl-chloride dissolved in 25 parts by volume of dry benzene are added dropwise with stirring at 25-30° over a period of 10 minutes. The reactants are then heated under reflux for 3 hours; 1.6 parts of triethylamine hydrochloride are filtered off. The yellow filtrate is washed with saturated sodium chloride solution, twice with 2N Na_2CO_3 solution, then again with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and the solvent is then evaporated under vacuum. 6 Parts of a solid residue are obtained and purified by vacuum distillation. The n-hexyl 3,5-di-t-butyl-4-hydroxybenzoate distills at 150-155° and 0.1 mm Hg pressure and melts at 70-72°. The yield of the pure product is 3 parts.

Example 11: n-Dodecyl 3,5-Di-t-butyl-4-hydroxybenzoate

2.78 Parts of n-dodecanol and 1.88 parts of triethylamine are dissolved in 50 parts by volume of dry benzene, and 5.0 parts of 3,5-di-t-butyl-4-hydroxybenzoyl-chloride dissolved in 25 parts by volume of dry benzene are added dropwise with stirring at 25-30° over a period of 10 minutes. The reactants are then heated under reflux for 3 hours. 1.85 Parts of triethylamine hydrochloride are filtered off. The yellow filtrate is washed with saturated $NaCl$ solution, twice with 2N Na_2CO_3 solution, then

again with saturated NaCl solution, dried over anhydrous Na₂SO₄, and the solvent evaporated under vacuum. 8 Parts of a solid residue are obtained. The residue is purified by vacuum distillation. The n-octyl 3,5-di-t-butyl-4-hydroxybenzoate distills at 189-193° and 1-2 microns and melts at 47-53°.

5 **EXAMPLE 15: Stabilization of Polypropylene**

10 Unstabilized polypropylene powder (Hercules PROFAX 6501) is thoroughly blended with 0.5% by weight of 2-(n-octadecylthioethyl) 3,5-di-t-butyl-4-hydroxyphenylacetate, made according to Example 1 hereinabove. The blended material is then milled on a two roller mill at 182° for 5 minutes, after which time the stabilized polypropylene is sheeted from the mill and allowed to cool.

15 The milled polypropylene sheet is then cut into small pieces and pressed for 7 minutes on a hydraulic press at 218° and 2000 pounds per square inch pressure. The resultant sheet of 25 mil thickness is then tested for resistance to accelerated aging in a forced draft oven at 149°. The resultant composition of 0.5% by weight of 2-(n-octadecylthioethyl) 3,5-di-t-butyl-4-hydroxyphenylacetate and polypropylene is stabilized against oxidative deterioration for 1000 hours. The unstabilized polypropylene deteriorates after only 3 hours.

20 25 In like manner as in this example, stabilized compositions of polypropylene are prepared having 0.5% by weight of a compound prepared according to each of the foregoing examples.

30 35 In a similar manner as in this example, stable compositions of polypropylene are prepared with 0.5% by weight of one compound according to each of the preceding examples together with 0.5% by weight of dilaurylthio-dipropionate. In some cases, the improvement is so remarkable that a synergistic effect is observed in the oven-aging test.

Example 13:Stabilization of a Resin Containing Elastomer

High impact polystyrene resin containing elastomer (i.e. butadiene-styrene) (Foster Grant, XI 516, unstabilized) is stabilized against loss of elongation properties by incorporation of 0.5% by weight of a stabilizer (Table I). Under the test conditions described hereinbelow, the stabilized resin retains from 50 to 65% of its original elongation properties, whereas the unstabilized resin retains only 15% of its elongation properties.

The unstabilized resin is dissolved in chloroform and the stabilizer then added, after which the mixture is cast on a glass plate and the solvent evaporated to yield a uniform film, which, upon drying, is removed and cut up and then pressed for 7 minutes at a temperature of 163° and a pressure of 2000 pounds per square inch into a sheet of uniform thickness (25 mil). The sheets are then cut into strips, approximately 4 x 0.5 inches. A portion of these strips is then measured for length of elongation in the Instron Tensile Tester (Instron Engineering Corporation, Quincy, Massachusetts). The remaining portion of the strips is aged in a forced draft oven for 6 weeks at 75° and thereafter tested for elongation.

Table I below shows two stabilized resins compared with an unstabilized resin.

20

TABLE I

Stabilizer Compound	Percent Elongation Retained	Stabilization Factor (Improvement over Blank)
n-Octadecyl 8-(3,5-di-t-butyl-4-hydroxyphenyl)propionate	65	4.3
2-(n-Octylthioethyl) 3,5-di-t-butyl-4-hydroxybenzoate	50	3.3
Blank (no stabilizer)	15	1

843985

14

EXAMPLE 16:

Diethylene Glycol Bis-[β -(3,5-di-t-butyl-4-hydroxyphenyl)propionate]

A mixture of 16.7 parts of 3-[β ,5-di-t-butyl-4-hydroxyphenyl]-propionic acid, 2.65 parts of diethylene glycol, 2.5 parts of para-toluene sulfonic acid monohydrate, and 300 parts by volume of benzene is refluxed until no further water separates.

After cooling, the mixture is diluted with 200 parts by volume of benzene and washed successively with the following: water, 0.5 N sodium hydroxide, water, and saturated aqueous sodium chloride. After drying with sodium sulfate and removal of the solvent at reduced pressure, 14.3 parts of a syrupy residue remain. The product, diethylene glycol bis-[β -(3,5-di-t-butyl-4-hydroxyphenyl)propionate], is obtained by triturating with aqueous ethanol, followed by methanol, then crystallizing once from each of these solvents in the order given. This yields the said product of constant melting point 90-91.5°.

Analysis:

	C	H	O
Calculated for $C_{38}H_{58}O_7$:	72.80%	9.32%	17.86%
Found:	72.62%	9.34%	18.18%

15

EXAMPLE 17

1,2-Propylene Glycol Bis-[β -(3,5-di-t-butyl-4-hydroxyphenyl)propionate]

A mixture consisting of 16.7 parts 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid, 1.90 parts propylene glycol, 2.5 parts para-toluene sulfonic acid monohydrate, and 300 parts by volume of toluene is refluxed until a constant quantity of water has been collected in the Dean-Stark water trap.

After cooling, the mixture is diluted with 300 parts by volume of benzene and washed successively with the following: water, 0.5 N sodium hydroxide, water and saturated sodium chloride. After drying over sodium sulfate, removal of the solvent under reduced pressure yields 1,2-propylene glycol bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (13.1 parts). This is purified by chromatographing through alumina. Elution with hexane results in the appearance of a minor amount of yellow oil which is followed by the desired product. It crystallizes spontaneously and has a melting point of 70°.

Analysis:

	C	H	O
Calculated for $C_{37}H_{56}O_8$:	74.45 %	9.45 %	16.08 %
Found:	74.23 %	9.72 %	16.15 %

H 16

15 EXAMPLE 18 Ethylene Glycol Bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]

A mixture consisting of 13.9 parts 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid, 1.24 parts ethylene glycol, 1.0 part para-toluene sulfonic acid monohydrate, and 300 parts by volume of benzene is refluxed until a constant amount of water has been separated by azeotropic distillation.

20 After cooling, the solution is extended with 100 parts by volume of benzene and washed with the following in succession: water, 0.33 N sodium hydroxide, 0.5 N sodium hydroxide, 5% hydrochloric acid, water, and finally with saturated sodium chloride. After drying over sodium sulfate, evaporation of the benzene gives 8.7 parts of ethylene glycol bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]. Crystallization from 95% ethanol gives the desired product of a melting point of 146-147°.

843985

Analysis:

Calculated for C₃₆H₅₄O₆: 74.18%

Found: 74.14%

C

H

9.33%

9.68%

SUPPLEMENTAL DISCLOSURE

The compounds described in the Principal Disclosure have been found to be stabilizers for a wide variety of organic material normally subject to deterioration. These 5 include synthetic organic polymeric substances such as vinyl resins formed from the polymerization of vinyl halides or from the copolymerization of vinyl halides with unsaturated polymerizable compounds, e.g., vinyl esters, α,β -unsaturated acids, α,β -unsaturated esters, α,β -unsaturated 10 ketones, α,β -unsaturated aldehydes and unsaturated hydrocarbons such as butadienes and styrene; poly- α -olefins such as polyethelene, polypropylene, polybutylene, polyisoprene and the like, including copolymers of poly- α -olefins; polyurethanes such as are prepared from polyols and organic 15 polyisocyanates; polyamides such as polyhexamethylene adipamide; polyesters such as polymethylene terephthalates; polycarbonates; polyacetols; polystyrene; polyethyleneoxide; and copolymers such as those of high impact polystyrene containing copolymers of butadiene and styrene and those formed by 20 the copolymerization of acrylonitrile, butadiene and/or styrene. Other materials stabilized according to the present invention includes lubricating oil of the aliphatic ester type, e.g., di-(2-ethylhexyl) azelate, penterythitol tetra-caproate and the like; animal and vegetable derived oils, e.g., linseed oil, fat, tallow, lard, peanut oil, cod liver 25 oil, canter oil, palm oil, corn oil, cotton seed oil and the like; hydrocarbon material such as gasoline, both natural and synthetic, diesel oil, mineral oil, fuel oil, cutting;

H

2/
-28-

fluids, waxes, resins and the like; fatty acids; soaps; and the like.

Particularly preferred compounds of the present invention are those wherein the acyl moiety is the 3-(3,5-di-5 t-butyl-4-hydroxyphenyl)propionate group. Typical of these are n-octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate; 2-(octadecylthio)ethyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and thio-bis-[ethylene 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate].

10 The following examples will serve to typify the nature of these compounds:

H

EXAMPLE 17

Neopentylglycol bis-[3-(3,5-

di-t-butyl-4-hydroxyphenyl)-propionate]

15 Methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate (21.1 parts), 3.12 parts neopentylglycol and 0.375 parts of sodium methylate are heated under nitrogen at 130° for 1 1/2 hours. The methanol thus formed is collected in dry-ice acetone cooled trap. After the theoretical amount of methanol 20 is collected, the reaction mixture is heated at 150°/0.05mm for 3 hours. At the end of this time, the material is dissolved in hexane and filtered. The filtrate is then concentrated and recrystallized from 95% ethanol and thoroughly dried to yield neopentylglycol bis-[3-(3,5-di-t-butyl-4-25 hydroxyphenyl)-propionate], m.p. 81-82°.

EXAMPLE 18

Ethylene glycol bis-(3,5-

di-t-butyl-4-hydroxyphenylacetate)

A mixture consisting of 13.2 parts of 3,5-di-t-butyl-30 4-hydroxyphenylacetic acid, 1.24 parts of ethylene glycol,

22
-24-

1.7 parts of p-toluene sulfonic acid monohydrate and 55 parts by volume of benzene are treated according to the procedure of Example 17. The washed and dried benzene solution obtained from the reaction mixture is evaporated to yield 9.3 parts of ethylene glycol bis-(3,5-di-t-butyl-4-hydroxy-phenylacetate) which is further purified by recrystallization, m.p. 116-117°.

19

EXAMPLE 21

H
10 2-(n-Octadecylthio)ethyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate

2-Hydroxyethyl n-octadecyl sulfide (8.26 parts) and 3.03 parts of triethylamine are dissolved in 75 parts by volume of dry benzene and 3.91 parts of 3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionyl chloride dissolved in 100 parts 15 by volume of dry benzene are added dropwise over a period of 10 minutes at 25-30°C. The reaction mixture is then heated for 3 hours and filtered. The filtrate is washed once with saturated sodium chloride solution, twice with 2N aqueous sodium carbonate solution and then once again with 20 saturated sodium chloride solution. After drying over sodium sulfate, the solvent is removed under reduced pressure to yield a syrup which is purified as a hexane solution by chromatography over alumina. Removal of the hexane then yields a syrup which crystallizes to yield the 25 product, m.p. 45-47°C.

20

EXAMPLE 22

Thio-bis-[ethylene 3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate]

Bis-(2-hydroxyethyl) sulfide (3.05 parts) and 6.76 parts of triethylamine are dissolved in 150 parts by volume of dry benzene and 17.0 parts of 3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionyl chloride dissolved in 200 parts

23

- 25 -

by volume of dry benzene are added and heated as in Example 21. The resulting benzene solution is filtered, dried and evaporated as therein described and the residue dissolved in hexane and purified by percolating through alumina (neutral, activity III). Removal of the solvent yields the product, thio-bis-[ethylene β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionate] as an oil which is soluble in hydrocarbons and gives the following analysis:

Calc. for $C_{38}H_{58}O_6S$: C, 70.93; H, 9.09; S, 4.01

10 Found: C, 70.88; H, 9.13; S, 3.23

EXAMPLE 21

H neo-Dodecyl β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionate

Methyl β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionate (29.2 parts), 18.6 parts of neo-dodecanol and 15 0.270 parts of sodium methylate are treated as described in Example 2. The reaction mixture is then dissolved in benzene, ether is added and the resulting solution washed successively with water and saturated aqueous sodium chloride solution and then dried over sodium sulfate. The solution is next filtered and the filtrate stripped of solvents under diminished pressure. The residue is distilled in vacuo to yield 13.7 parts of neo-dodecyl β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionate, b.p. 110°/0.20 mm - 111.5°/0.15 mm.

25 Calc. for $C_{28}H_{56}O_3$ C, 77.97; H, 11.23

Found: C, 78.17; H, 11.23

H

EXAMPLE 24

Methyl p-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate

To 500 parts by volume of dry t-butyl alcohol in a flask fitted with mechanical stirrer, inert gas inlet, thermometer, condenser and dropping funnel are added 2.1 parts of potassium metal. After the ensuing reaction is complete, there are added 57.5 parts of 2,6-di-t-butyl-phenol, followed rapidly by 17.7 parts of methylacrylate. The stirred reaction mixture is heated to 50°C for 13 hours and allowed to cool. The solvent is removed under reduced pressure and the residual mass neutralized by addition of dilute hydrochloric acid. This mixture is then extracted with two portions of 200 parts by volume each of ethyl ether. The combined ethereal extracts are washed with two portions of 100 parts by volume each of water and then dried over anhydrous sodium sulfate. The ether layer is removed by filtration and concentrated on a steam bath. The residual oily mass is then vacuum distilled. The fraction collected at 120-130°C/0.1 mm crystallizes upon standing to yield methyl p-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate, m.p. 55.5-56.5°C. Recrystallization from hexane yields a white solid, m.p. 56.0-56.5°C.

	C	H	Saponification Equivalent
Calc. for $C_{18}H_{30}O_3$:	5.35	0.51	100.4
Found:	5.37	0.49	101.4

In a similar fashion, the corresponding alkyl esters are obtained from the respective alkyl acrylates: ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl.

843985

deeyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, behenyl, docosyl, tricosyl and tetracosyl.

Either benzyltrimethylammonium methoxide or sodium methoxide may be substituted for potassium t-butoxide in this example.

Alternatively, a slurry of 3.0 parts of potassium hydroxide in 500 parts by volume of t-butyl alcohol is used in the place of potassium (as the alcoholate). A somewhat lower yield of the product ester is realized by this method.

23

EXAMPLE 24

Dodecyl β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionate

To 5.0 parts by volume of dry t-butyl alcohol is added 0.5 parts of potassium metal. Upon completion of the ensuing reaction, there is added 42.3 parts of 3,5-di-t-butyl phenol and 57.0 parts of isopropyl acetate in rapid succession. The resulting mixture is heated at reflux for 5 hours and then allowed to cool. The solvent is removed under reduced pressure and the residual base neutralized with very dilute hydrochloric acid. The reaction mixture is extracted with two portions of 5.0 parts by volume of 1:1 ethyl ether:petroleum ether and the combined extracts washed with two portions of 100 parts by volume of water. The extract is then dried over anhydrous sodium sulfate, the drying agent removed by filtration and the etheral solution concentrated with a final temperature of 200° at a pressure of 0.1 mm to yield dodecyl β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionate.

26
-26-

Calc. for $C_{18}H_{30}O_3$: C, 74.1%; H, 11.4%
 Found: C, 77.0%; H, 11.4%

24
EXAMPLE 24

Octadecyl α -(2,5-di-t-butyl-4-hydroxyphenyl)-isobutyrate

1. To 200 parts by volume of dry t-butyl alcohol in suitable flask fitted with mechanical stirrer, inert gas inlet, thermometer, condenser and dropping funnel is added 20.4 parts of potassium t-butoxide, 51.2 parts of 2,5-di-t-butylphenol and 50 parts by volume of triethylene glycol dimethyl ether. The dark green solution is stirred and a solution of an equimolar portion of ethyl α -bromo- α -methyl-propionate in 50 parts of t-butyl alcohol is added dropwise over 20-30 minutes. After addition is complete, the reaction is refluxed for 1 hour, the solution being neutral. The reaction mixture is poured into water and extracted with ether. The ethereal solution is washed with water and dried and the ether removed by distillation, the product being isolated by vacuum distillation.

2. By substitution ethyl α -bromo-propionate for ethyl α -bromo- α -methylpropionate in the procedure of this example there is obtained ethyl α -(2,5-di-t-butyl-4-hydroxyphenyl)propionate.

3. Calc. for $C_{18}H_{30}O_3$: C, 74.1%; H, 9.1%
 Found: C, 77.0%; H, 9.1%

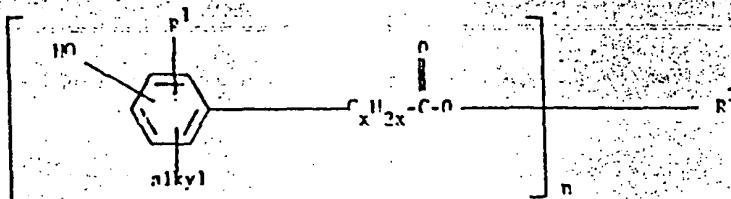
4. By employing 2-methyl-4-t-butylphenol in place of 2,5-di-t-butylphenol in the procedure of this example methyl α -(2-methyl-4-hydroxy-3-t-butylphenyl)-propionate is obtained b.p. 130-140°/0.01 mm.

b.) A solution of 16 parts of ethyl α -(4-hydroxy-3,5-di-t-butylphenyl)-isobutyrate, 15.5 parts of n-octadecyl alcohol and 0.5 parts of sodium methylate in 15¹ parts by volume of o-dichlorobenzene is distilled under a nitrogen atmosphere until the vapor temperature reaches and remains at the boiling point of o-dichlorobenzene (130-135°). The solution is then refluxed for 6 hours, cooled and neutralized with a few drops of acetic acid. The solvent is removed under vacuum on a water bath and the product, octadecyl α -(4-di-t-butyl-4-hydroxyphenyl)isobutyrate, after two recrystallizations from methanol melts at 16-46°. The yield is 57%.

Similarly a solution of 20 parts of ethyl α -(4-hydroxy-3,5-di-t-butylphenyl)-propionate, 17.35 parts of n-octadecyl alcohol and 0.5 parts of sodium methylate in 15¹ parts by volume of dry toluene is distilled under a nitrogen atmosphere until the vapor temperature reaches and remains at the boiling point of toluene. The solution is then cooled and neutralized with acetic acid. The solvent is removed under vacuum on a water bath and the product, octadecyl α -(3,5-di-t-butyl-4-hydroxyphenyl)-propionate, after two recrystallization from methanol melts at 46-50°. The yield is 53%.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A compound of the formula:



in which

p^3 is hydrogen or alkyl,

x is zero or an integer of from 1 to 6,

n is 1 or 2, and

when n is 1, R^2 is

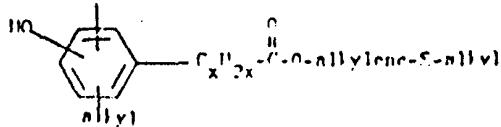
- (i) alkyl of 6 to 24 carbon atoms,
- (ii) alkylthioalkyl of 8 to 24 carbon atoms, or
- (iii) hydroxyalkylthioalkyl of 8 to 24 carbon atoms,

provided that when x is zero and R^2 is alkyl, the alkyl group has from 6 to 11 carbon atoms, the hydroxyl group is in the 4-position, R^1 is *t*-butyl and R^1 and "alkyl" are in the 3- and 5-positions; or

when n is 2, R^2 is

- (i) alkylene of 2 to 6 carbon atoms,
- (ii) alklenethioalkylene of 2 to 12 carbon atoms, or
- (iii) alkyleneoxynalkylene of 4 to 24 carbon atoms.

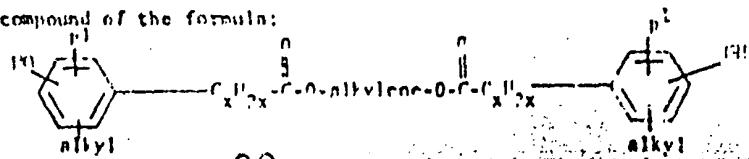
2. A compound of the formula:



In which ρ^1 is hydrogen or alkyl, "allylene- ρ -alkyl" has from 2 to 12 carbon atoms, and

x has a value of from 0 to 1.

3. A compound of the formula:



in which R^1 is hydrogen or alkyl,

"alkylene" has from 2 to 6 carbon atoms, and

x has a value of from 0 to 6.

4. A compound as claimed in claim 1 wherein n is 1, x is zero, the hydroxyl is in the 4-position, R^1 and "alkyl" are t-butyl groups in the 3- and 5-positions and R^2 is alkyl of 6 to 11 carbon atoms.

5. The compound of claim 4 which is n-hexyl 3,5-Di-t-butyl-4-hydroxybenzoate.

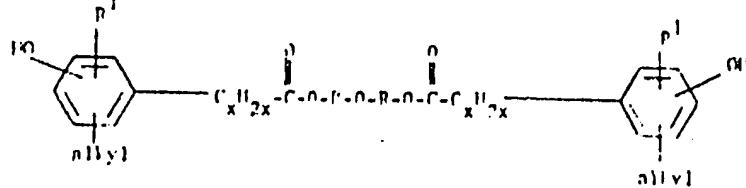
6. A compound as claimed in claim 1 wherein n is 1, x is 1, R^1 and "alkyl" are t-butyl groups in the 3- and 5-positions and the hydroxyl is in the 4-position.

7. A compound as claimed in claim 1 wherein n is 1, x is 2, R^1 and "alkyl" are t-butyl groups in the 3- and 5-positions and the hydroxyl is in the 4-position.

8. A compound as claimed in claim 2 in which the hydroxyl group is in the 4-position on the benzene ring, R^1 and the "alkyl" attached to the benzene ring are t-butyl groups in the 3- and 5-positions and x is zero, 1 or 2.

9. A compound as claimed in claim 3 wherein each hydroxyl is in the 4-position, R^1 and "alkyl" are t-butyl groups in the 3- and 5-positions and x is zero, 1 or 2.

10. A compound of the formula:



in which R is alkylene of 2 to 6 carbon atoms, R^1 is hydrogen or alkyl and x is a value of from zero to 6.

1:1

11. A compound as claimed in claim 10 wherein each hydroxyl is in the 4-position, R¹ and "alkyl" are t-butyl groups in the 3- and 5-positions and x is zero, 1 or 2.
12. A compound of claim 8 which is 2-(n-octylthioethyl) 3,5-di-t-butyl-4-hydroxybenzoate.
13. A compound of claim 2 which is 2-(n-Octylthioethyl) 3,5-di-t-butyl-4-hydroxyphenylacetate.
14. A compound of claim 8 which is 2-(n-Octadecylthioethyl) 3,5-di-t-butyl-4-hydroxyphenylacetate.
15. A compound of claim 8 which is 2-(n-Octadecylthioethyl) 3,5-di-t-butyl-4-hydroxybenzoate.
16. A compound as claimed in claim 1 in which n is 1 and R² is hydroxy alkylthioalkyl of 8 to 24 carbon atoms.
17. A compound of claim 16 which is 2-hydroxyethylthio-2'-ethyl (3,5-di-t-butyl-4-hydroxy)benzoate.
18. The compound as claimed in claim 1 wherein n is 2 and R² is alkylene thio-alkylene of 2 to 12 carbon atoms.
19. The compound of claim 18 which is 2,2-thiodiethyl bis-(3,5-di-t-butyl-4-hydroxyphenylacetate).
20. The compound of claim 11 which is diethylene glycol bis-[3-(3,5-di-t-butyl-4-hydroxy-phenyl)propionate].
21. The compound of claim 9 which is 1,3-propylene glycol bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate].
22. The compound of claim 9 which is ethylene glycol bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate].
23. The compound of claim 1 which is n-octadecyl 3,5-di-t-butyl-3-hydroxyphenyl-acetate.

843985

24. The compound of claim 1 which is n-octadecyl 8-(3,5-di-t-butyl-4-hydroxyphenyl)propionate.